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VIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

NOTE ON TRIBROMMONONITROBENZOL.

BY C. LORING JACKSON AND W. B. BENTLEY.

Presented May 13, 1891.

THE results of experiments on the behavior of tribromtrinitrobenzol and tribromdinitrobenzol with various reagents have been described in a number of papers from this Laboratory. For the sake of completeness, we felt it necessary to include the tribrommononitrobenzol in our investigation, and were the more inclined to do this as we hoped that it might throw some light on the replacement of bromine by hydrogen, so often observed in our work with the trinitro and dinitro compounds. This hope has not, however, been fulfilled, as no such replacement of bromine by hydrogen was observed, and the tribrommononitrobenzol has proved to be so inert with various reagents, that it deserves only the short investigation the results of which are given in this paper.

The tribrommononitrobenzol used in this work was prepared by boiling symmetrical tribrombenzol (melting point 119°) for fifteen minutes with a nitric acid made by adding to fuming nitric acid (specific gravity 1.51) one quarter of its volume of common strong nitric acid (specific gravity 1.38). The greater part of the tribrommononitrobenzol separated as the mixture cooled, and the rest was obtained by the addition of water to the acid mother liquor. This process gave better results than when acetic acid was used to dilute the fuming nitric acid according to the method given by V. von Richter.*

Action of Tribrommononitrobenzol with Sodic Ethylate.

The tribrommononitrobenzol melting at 125° was acted on by hot sodic ethylate giving a substance which we found it convenient to prepare as follows: — 5 gr. of tribrommononitrobenzol dissolved in benzol were mixed with an alcoholic solution of the sodic ethylate from 1 gr. of sodium, heated on the water bath just below boiling for some time, and then allowed to stand at a temperature a little above the ordinary for several hours. The red solution thus obtained was filtered from a precipitate which had formed, (this gave a test for bromide with argentic nitrate,) diluted with water, and acidified with dilute sulphuric acid, after which the benzol was separated from the aqueous liquid; this was extracted with ether, and the combined extracts from the organic solvents purified by crystallization from alcohol until the constant melting point 91° was reached. Sometimes a black tarry product was obtained from the reaction, instead of the white crystals formed if the process had gone well. This tarry mass was worked up most conveniently by distillation with steam, followed by crystallization of the steam distillate from alcohol. The pure substance was dried at about 70°, and analyzed with the following results: —

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* Ber. d. ch. G., VIII. 1426.

I. 0.1900 gr. of the substance gave by the method of Carius 0.2181 gr. of argentic bromide.

II. 0.3800 gr. of the substance gave 15.9 c. c. of nitrogen at a temperature of 22° and a pressure of 756.5 mm.

	Calculated for $C_6H_2Br_2NO_2OC_2H_5$.	Found.	
		I	II.
Bromine	49.22	48.85	
Nitrogen	4.31		4.72

The substance is therefore dibromnitrophenetol, and was formed by the replacement of one atom of bromine by the ethoxy radical.

Properties. — The dibromnitrophenetol crystallizes in bundles of prisms, which are usually somewhat flattened and terminated by a basal plane, also occasionally showing with this two other planes at an obtuse angle to each other. It is white, but turns brown on exposure to the air; melting point 91°; essentially insoluble in cold water, perhaps very slightly soluble in hot; alcohol disolves it sparingly when cold, freely when hot; more soluble in methyl than in ethyl alcohol; very freely soluble in benzol, chloroform, acetone, or carbonic disulphide; freely soluble in ether; slightly soluble in cold glacial acetic acid, soluble in hot; very slightly soluble in ligroine. The best solvent for it is hot alcohol. It distils with steam. Strong sulphuric acid has no action in the cold, but when hot gradually forms a black solution; cold nitric acid has no action on it, but when hot dissolves it, depositing crystals on cooling, which seem by their melting point to be the unaltered substance; strong hydrochloric acid seems to have no action, whether hot or cold; sodic hydrate seems not to act upon it.

Action of other Reagents on Tribrommononitrobenzol.

Sodic methylate behaved in much the same way as the sodic ethylate, except that it was necessary in this case to heat for a longer time, and even after this a certain amount of tribrommononitrobenzol was apt to be left unaltered. The product after crystallization from alcohol showed the constant melting point 104°, but its analyses gave percentages of bromine differing from those corresponding to dibromnitroanisol by about one per cent. The cause of this is probably the same as that of the similar want of agreement between the calculated and observed percentages in the case of the bromdinitroresorcine dimethylether;* but we have not thought the substance of sufficient importance to try to obtain better analytical results, which, to judge by our work on the bromdinitroresorcine dimethylether, would be a matter of great difficulty.

From these experiments it appears that the tribrommononitrobenzol acts with sodic alcoholates less easily than the tribromdinitrobenzol, which is attacked by them in the cold forming the ethers of bromdinitroresorcine, whereas it is necessary to heat the mononitro compound to bring about any action. When the tribromdinitrobenzol is heated with an alcoholate, the third atom of bromine is replaced by hydrogen and an ether of the dinitroresorcine is formed, but we found no trace of any action of this sort with the mononitro compound. It is to be noted, too, that only one atom of bromine is removed from the mononitro, but two from the dinitro compound.

The inertness of tribrommononitrobenzol as compared with the corresponding dinitro compound is made even more evident by the study of the action of aniline upon it. This substance converts tribromdinitrobenzol into trianilidodinitrobenzol, when heated with it for a short time, whereas the corresponding trinitro compound is formed in the cold; from the mononitro substance we were unable to obtain any anilido compound, even after heating for some time to the boiling point of aniline; a little aniline bromide was formed, it is true, but almost all of the tribrommononitrobenzol was recovered unaltered, as recognized by its melting point and very characteristic crystalline form.

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* These Proceedings, XXV. 175.

No better result was obtained with sodium malonic ester, which acts on the dinitro and trinitro compounds in the cold, but even after boiling for some time with the tribrommononitrobenzol yielded only a very small quantity of sodic bromide, while almost all of the tribrommononitrobenzol was recovered unaltered.